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Title:

CATALYTIC CONVERSION OF PROPENE INTO HIGHER BOILING HYDROCARBONS ;

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DE1248845, DE1443074, GB935718, NL105779C, NL126095C, NL251684, US3149180 ;

ABSTRACT:

COMPLETE SPECIFICATION

ERRATA

SPECIFICATION NO. 878,035

5   Page 2, line 115, *for* "catalvtically" *read* "catalytically"

Page 3, line 7, *for* "silic" *read* "silica"

10   Page 4, Table 1, 1st Column, 6th Entry, *for* "1-pentanes" *read* "1-pentenes"

Page 8, line 10, *after* "pressure" *insert* "colon"

15   Page 8, *delete lines 23 to 30 inclusive and substitute*

"bulk volume of catalyst	800 cm^3
temperature	500 C.
air rate	5 litres (S.T.P.)/h
20 | steam rate | 0.1 kg/h " |

Page 12, line 49, *for* "factor" *read* "factors"

Page 13, line 17, *for* "temperatures" *read* "temperature"

25   Page 13, line 48, *for* "redily" *read* "readily"

Page 13, line 68, *for* "rection" *read* "reaction"

Page 14, line 49, *for* "olefinc" *read* "olefinic"

30   Page 14, line 68, *after* "any" *insert* "one"

Page 15, line 48, *for* "cribled" *read* "cribed"

40   and/or arsenides of the metals of the left-hand column of Group VI (chromium, molybdenum, tungsten) and/or one or more sulphides, selenides, tellurides, antimonides and/ formed besides the hydrocarbons that have the   85
same number of carbon atoms per molecule.
For example propene may be converted into
higher-boiling branched olefins and/or para-

[*Price 3s. 6d.*]

PATENT SPECIFICATION

DRAWINGS ATTACHED

878,035

Index at acceptance:—Class 2(3), B1(D: H: I: L).

International Classification:—C07c.

COMPLETE SPECIFICATION

Improvements in or relating to the Catalytic Isomerization of Olefinic Hydrocarbons

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The invention relates to a process for the catalytic hydro-isomerization of hydrocarbons and in particular to a process for the catalytic conversion of unbranched or sparsely branched hydrocarbons into hydrocarbons having a branched or more highly branched carbon chain respectively.

It is already known that low-molecular weight straight-chain hydrocarbons having four or more carbon atoms may be isomerized to branched-chain hydrocarbons having the same number of carbon atoms, or vice versa, by passing the hydrocarbons over inorganic adsorbents or over sulphidic or oxidic hydrogenation or dehydrogenation catalysts, in particular the sulphides of the heavy metals of Groups VI, VII and VIII of the Periodic Table, at elevated temperatures and at high total pressures; the hydrogen partial pressure should, however, be very low, viz. 5% of the total pressure or even less. Suitable adsorbants are alumina, silica gel, zinc oxide, active carbon and silicates, and such compounds may also serve as carriers or as binders for the said hydrogenation or dehydrogenation catalysts.

It has now been found that when isomerizing unbranched or sparsely branched olefins in the presence of hydrogen or a hydrogen-containing gas and by means of a solid acidic containing isomerization catalyst containing one or more sulphides, selenides, tellurides, antimonides and/or arsenides of the metals of the left-hand column of Group VI (chromium, molyb-denum, tungsten) and/or one or more sul-phides, selenides, tellurides, antimonides and/ phides, selenides, tellurides, antimonides and/

or arsenides of the metals of Group VIII (iron, cobalt, nickel and the noble metals) of the Periodic Table, very high yields of branched or more highly branched hydrocarbons respectively may be obtained.

Thus the present invention relates to a process for the catalytic conversion of unbranched or sparsely branched hydrocarbons into hydrocarbons having a branched or more highly branched carbon chain respectively, which comprises contacting an olefinic starting material at elevated temperature and pressure and in the presence of hydrogen or a hydrogen-containing gas with a solid acidic isomerization catalyst on which are supported one or more sulphides, selenides, tellurides, antimonides and/or arsenides of the metals of the left-hand column of Group VI and/or one or more sulphides, selenides, tellurides, antimonides and/or arsenides of the metals of Group VIII of the Periodic Table.

The term olefinic starting material as used in the present specification designates a starting material that consists of one or more un-branched or sparsely branched olefins or of a mixture of one or more of such olefins with one or more other substances, such as non-olefinic hydrocarbons. The olefins may or may not contain cyclic substituents.

The olefins which occur in the starting material used in the process of the invention are mainly converted into branched or more highly branched olefins and/or paraffins. Generally the olefins are to a large extent converted into hydrocarbons with the same number of carbon atoms per molecule. However, depending on the reaction conditions, the catalyst and the feed stock, smaller or larger amounts of hydrocarbons with a different number of carbon atoms per molecule may be formed besides the hydrocarbons that have the same number of carbon atoms per molecule. For example propene may be converted into higher-boiling branched olefins and/or para-

ffins, branched hydrocarbons having 4, 5 and 6 carbon atoms per molecule being predominantly formed.

The degree of saturation of the final product is dependent on the composition of the catalyst and the reaction conditions, in particular the space velocity. Further, the catalyst is capable of converting into saturated hydrocarbons both the olefins present in the starting material and the (mainly branched) olefins formed during the reaction. A lower space velocity results in a more drastic hydrogenation of the unbranched olefins present in the feed or formed during the process. The liquid hourly space velocity of the fresh starting material to be converted generally varies from 0.5 litre to 20 litres of liquid hydrocarbons per hour per litre of catalyst (1/h.1), although lower or higher velocities may also be used.

If the reaction conditions are such that there is no complete hydrogenation of the reaction product, the product may, if desired, be subsequently catalytically hydrogenated in a manner known per se, for instance by means of a catalyst containing nickel, platinum, cobalt sulphide-molybdenum sulphide or cobalt oxide-molybdena. This hydrogenation will generally not be carried out when the reaction product is to be used as motor gasoline or as a motor gasoline component, but it is sometimes advantageous when the reaction mixture is to be extracted for recovering aromatics present therein.

The process according to the invention may be used with particular advantage when olefinic starting materials also containing diolefins and/or alkynes are employed. The active life of conventional solid acidic isomerization catalysts hitherto used has been found to be very short, particularly in the isomerization of such feedstocks containing diolefins and/or alkynes, presumably due to the formation of diene polymers and the like, which deposit on the catalyst and rapidly reduce its activity. In the process according to the invention, however, any dienes and alkynes present are selectively hydrogenated to mono-olefins, which may then participate in the isomerization reaction (and any subsequent hydrogenation reaction). This not only extends the life of the catalyst but also leads to a higher yield of branched hydrocarbons. Similarly, when olefinic starting materials are employed not containing diolefins and alkynes, the life of the present catalysts is more favourable than the life of the catalysts hitherto used.

The process according to the invention is particularly suitable for the isomerization of olefins having from 3 to 8 carbon atoms per molecule, preferably from 4 to 8 carbon atoms per molecule. Thus, preferred starting materials consist of or contain one or more olefins having from 3 to 8, particularly from 4 to 8 carbon atoms per molecule. Propene is a very suitable starting material. Those

products of the present process that boil substantially within the gasoline boiling range are particularly suitable as premium motor fuels or components for premium motor fuels.

Particularly suitable starting materials are the gasolines and gasoline fractions that are obtained by catalytic cracking of petroleum fractions. Such gasolines have a relatively high olefin content, as a result of which these gasolines, and particularly the lower-boiling fractions thereof have desirable high F—1 octane numbers although on the other hand they have the drawback of a very high sensitivity.

By sensitivity is meant the difference in octane number determined by the Research Method (F—1) and the octane number determined according to the Motor Method (F—2). The sensitivity is important because components of premium motor gasolines nowadays preferably should have minimum sensitivity as well as a high F—1 octane number.

By a conventional hydrogenation of such gasolines or gasoline fractions, in which the olefines are converted into the corresponding saturated compounds, the sensitivity is substantially improved but on the other hand there is the drawback of a marked lowering of the F—1 octane number.

However, by using the specific catalysts according to the present invention for the treatment of such gasolines, products are obtained which have a high F—1 octane number which is only slightly reduced from that of the untreated gasolines and show a greatly improved sensitivity. Such products are, therefore, very valuable premium motor fuels or premium motor fuel components. For this reason gasolines obtained by catalytic cracking (and in particular the lighter fractions thereof. having an upper cutting point between 80° C. and 130° C.) are preferred starting materials for the process according to the present invention.

Thus a light catalytically cracked gasoline, after treatment according to the present invention, may be mixed with one or more other gasoline components e.g. a higher-boiling fraction of a gasoline obtained by catalytic reforming and/or with the desulphurized and catalytically reformed intermediate fraction of a gasoline obtained by catalytic cracking. Such mixtures have very high F—1 octane numbers and very low sensitivity.

The presence of so-called acidic isomerization catalysts in the composite catalysts of the present invention ensures the selective isomerization of the olefins in the feed. By these catalysts are meant those which, with butter yellow indicator (dimethyl yellow, i.e. C_6H_5—$N{=}N$—C_6H_4—N—$(CH_3)_2$) and other still weaker basic indicators, show a colour change indicative of an acid medium.

Suitable acidic isomerization catalysts on which the metal sulphide, selenide, telluride, antimonide and/or arsenide components are

supported are, for instance, mixtures of silica and alumina, such as silica-alumina cracking catalysts, mixtures of silica and zirconium dioxide, mixtures of boron trioxide and alumina, mixtures of boron trioxide and silica, and mixtures of alumina and halogen, such as alumina and fluorine. The silic-alumina catalysts in particular those having a silica content of at least 60% by weight, are preferred. Among the sulphides, selenides, tellurides, antimonides and arsenides of the metals of the left-hand column of the Group VI and/or of the metals of Group VIII of the Periodic Table, the sulphides and in particular nickel sulphide and/or cobalt sulphide are preferred.

The quantities of metal sulphides, selenides, tellurides, antimonides and/or arsenides applied to the acidic isomerization catalyst may vary within wide limits and are generally in the range of from 0.5 to 15% by weight, based on the total catalyst. Thus for example, a catalyst containing silica and alumina and having a silica content of at least 60% by weight (based on the total catalyst) and on which is supported 1 to 10% by weight of nickel sulphide (based on the total catalyst) is excellently suitable for use in the process of the invention. The metal sulphide, selenide, telluride, antimonide and/or arsenide component may be incorporated with the acidic isomerization catalyst by any known method, for example, a metal sulphide may be applied by impregnating the acidic catalyst (which may or may not have been treated with a steam-air mixture at fairly high temperatures) with a solution of a salt of the corresponding metal, for instance, nickel nitrate, followed by drying, calcining and finally sulphiding with e.g. hydrogen sulphide or a gas containing hydrogen sulphide.

The catalysts used in the process of the invention are found to have an excellent activity, even at the preferred relatively low operating temperatures.

The olefinic starting material is contacted with the catalyst at elevated temperature. The temperature at the inlet of the first reactor (which may be the only one) is generally in the range of from 100° C. to 500° C., preferably from 200° C. to 500° C. and in particular from 200° C. to 400° C. or—for catalytically cracked gasolines or fractions thereof—from 250° C. to 450° C.

The conversion is carried out in the presence of hydrogen and/or a hydrogen containing gas and at elevated pressure, preferably at a total pressure in the range of from 10 to 100 atm., particularly in the range of from 20 to 60 atm. Total pressures exceeding 100 atm. are preferably not used since the higher the pressure the lower is the yield of branched compounds. The hydrogen partial pressure may vary within wide limits. However, it should be at least 5% and preferably at least 50% of the total pressure. Pure hydrogen may be used, but hydrogen-containing gases with a hydrogen partial pressure between 50 and 95% of the total pressure, such as the hydrogen-rich gases formed in reforming hydrocarbon oils, are also quite suitable.

It is preferred that the reaction mixture is completely or substantially completely in the vapour phase during the conversion reaction.

The process according to the present invention will now be illustrated by a number of Examples (Examples I—V) and compared with other processes (comparative Examples A—E). All these experiments were carried out in laboratory equipment, using about 100 cm^3 catalyst in each experiment, the catalyst being arranged in the form of a single fixed bed. All reactions were carried out in the vapour phase.

EXAMPLE I

A mixture of hexene-1 and hydrogen (molar ratio hydrogen/hydrocarbon = 4 : 1) was passed over an acidic isomerization catalyst consisting of 83.8% by weight of silica, 11.4% by weight of alumina and 4.8% by weight of nickel sulphide at a pressure of 20 kg/sq. cm., at an inlet temperature of 320° C. and a liquid hourly space velocity of 2 1/h.1.

The results obtained after the test periods indicated had lapsed, are summarized in Table I. The reaction product was nearly completely saturated.

The C_6 + fractions were completely hydrogenated and the F—1—0 octane numbers of the resultant products were determined. These octane numbers are also given in Table I.

TABLE I

Feed	hexene-1			
Catalyst	silica-alumina-nickel sulphide			
test period in hours	1.6	2.7	4.1	6.3
Composition of final product, % by weight				
methane	0.2	0.3	0.2	0.2
ethene and ethane	0.3	0.4	0.2	0.2
propene and propane	2.3	2.5	2.0	1.8
i-butenes and i-butane	13.3	13.4	12.0	10.9
n-butenes and n-butane	2.0	2.0	1.6	1.6
i-pentanes and i-pentane	12.8	13.0	12.0	11.5
n-pentene and n-pentane	0.3	0.4	0.3	0.2
2,2-dimethylbutene and 2,2-dimethylbutane	0.1	0.2	—	—
2,3-dimethylbutenes and 2,3-dimethylbutane	9.1	9.4	9.9	10.3
2-methylpentenes and 2-methylpentane	32.0	32.2	33.4	34.8
3-methylpentenes and 3-methylpentane	19.7	19.6	21.0	21.4
n-hexenes and n-hexane	2.5	2.3	3.1	2.9
higher hydrocarbons	5.4	4.3	4.3	4.2
yield $C_5{}^+$ fraction, % by weight	82	81	84	85
F—1—0 octane number of the saturated $C_5{}^+$ fraction	79	79	78	79

COMPARATIVE EXAMPLE A

A mixture of hexene-1 and hydrogen (molar hydrogen/hydrocarbon ratio = 4 : 1) was passed
5 over an acidic isomerization catalyst consisting of 88% by weight of silica and 12% by weight of alumina at a total pressure of 20 kg/sq. cm., an inlet temperature of 320° C. and a liquid hourly space velocity of 2 l.h/1.
10 The results obtained after the test periods indicated had lapsed are summarized in Table II. The reaction product was nearly completely saturated.

The $C_3{}^+$ fractions were again completely hydrogenated and the F—1—0 octane 15 numbers of the resultant products were determined. These octane numbers are also given in Table II.

TABLE II

Feed	Hexene-1		
Catalyst	silica-alumina		
test period in hours	1.5	3.7	6.4
composition of final product, % by weight			
methane	0.2	0.3	0.2
ethene and ethane	0.1	0.2	0.2
propene and propane	0.8	0.8	0.6
i-butenes and i-butane	1.3	0.8	0.6
n-butenes and n-butane	0.7	0.6	0.6
i-pentenes and i-pentane	1.5	0.8	0.8
n-pentenes and n-pentane	0.4	0.4	0.6
2,2-dimethylbutenes and 2,2-dimethylbutane	0.2	0.2	0.2
2,3-dimethylbutenes and 2,3-dimethylbutane	3.9	1.9	1.6
2-methylpentenes and 2-methylpentane	23.2	17.9	14.0
3-methylpentenes and 3-methylpentane	15.5	11.3	9.3
n-hexenes and n-hexane	49.4	63.3	70.1
higher hydrocarbons	2.8	1.5	1.2
yield C_5 + fraction, % by weight	97	97	98
F—1—0 octane number of the saturated C_5 + fraction	50	42	39

Comparison of Tables I and II shows that in the conversion of hexene-1 by means of a silica-alumina-nickel sulphide catalyst a sub-
5 stantially higher yield of branched hydrocarbons was obtained than in the conversion of the same feed by means of a silica-alumina catalyst containing no nickel sulphide.

The activity of the catalyst used in Experi-
10 ment I (according to the invention) remained practically constant unlike the catalyst without nickel sulphide, used in comparative Experiment A, i.e. the catalyst life of the former catalyst was better.

COMPARATIVE EXAMPLE B   15
Experiment I was repeated with n-hexane as the starting material instead of hexene-1. The same conditions and the same catalyst were used.

Table III shows the results obtained.   20

TABLE III

Feed	n-hexane
Catalyst	silica-alumina-nickel sulphide
test period, hours	6
composition of final product in % by weight	
methyl pentanes	0.1
n-hexane	99.9

This Table shows that with n-hexane only a very slight conversion into branched hydrocarbons was obtained.

COMPARATIVE EXAMPLE C

Two further tests were carried out, use being made in both cases of a silica-alumina cracking catalyst as the acidic isomerization catalyst. In the first of these two experiments nickel oxide, and in the second, platinum, was incorporated on this carrier, instead of the metal compounds used according to the process of the invention.

A mixture of hexene-1 and hydrogen (molar hydrogen/hydrocarbon ratio = 4 : 1) was passed over each of these catalysts at an inlet temperature of 320° C., a pressure of 20 atm. and a liquid hourly space velocity of 2 1/h.1.

The results of these tests are summarized in the following Table IV. The duration of the test was one hour in all cases. All the resulting final products were found to be completely saturated.

The F—1—0 octane number of the C_5^+ fraction obtained in the first test (with cracking catalyst + nickel oxide) was also determined and is given in the Table.

TABLE IV

Feed	Hexene-1	Hexene-1
Catalyst	silica—82.7 alumina—11.9 nickel oxide—6.0	silica—87.1 alumina—11.9 platinum—1.0
Composition of the final product in % by weight		
methane	0.7	—
ethane	0.7	—
propane	4.3	—
i-butane	11.1	—
n-butane	4.1	—
1-methyl butane	8.8	—
n-pentane	2.6	—
2,2-dimethyl butane	1.2	—
2,3-dimethyl butane	3.9	—
2-methyl pentane	21.0	} 0.5
3-methyl pentane	12.2	
n-hexane	25.2	99.5
higher hydrocarbons	4.2	
yield of $C_5{}^+$ fraction in % by weight	79	
F—1—0 octane number of the $C_5{}^+$ fraction	61	

The Table shows that branched hydrocarbons were admittedly formed when the silica-alumina-nickel oxide catalyst was used, but to a substantially lesser extent than when using the catalysts according to the process of the invention (Example I, Table I).

In the second test only small quantities of branched hydrocarbons were obtained, which demonstrates the unsuitability of the platinum containing catalyst for the isomerization of hexene-1.

COMPARATIVE EXAMPLE D

Another test was carried out, in which a mixture of hexene-1 and hydrogen was passed over a catalyst consisting of a non-acid carrier, viz. alumina on which cobalt sulphide-molybdenum sulphide was incorporated. The reaction conditions used in the latter case were: inlet temperature: 380° C., pressure: 36 atm., liquid hourly space velocity: 2 1/h.1, hydrogen/hydrocarbon molar ratio = 8:1.

The results are given in Table V.

TABLE V

Feed	hexene-1
Catalyst	alumina : 84 cobalt sulphide : 5 molybdenum sulphide : 11
Composition of final product, % by weight	
2-methyl pentane	5.1
3-methyl pentane	4.3
n-hexane	90.6

Table V shows that the non-acidic catalyst is unsuitable for the isomerization of hexene-1.

EXAMPLE II

In a further example of the process of the present invention, n-butene was used as the starting material. This material was passed over a nickel sulphide containing acidic isomerization catalyst, having the following composition: 82.3% by weight alumina, 11.2% by weight silica, 6.5% by weight nickel sulphide. The reaction conditions were: pressure 20 kg/cm², inlet temperature: 320° C., liquid hourly space velocity: 2.0 1/h.l., molar ratio H_2/hydrocarbon: 4:1.

The catalyst had been obtained in the following way:

A powdery silica-alumina cracking catalyst was mixed with 2% by weight of stearic acid and formed into 3×3 mm pellets. The stearic acid was burned away by calcining in air at 500° C. Subsequently a steam-air mixture was passed over the catalyst for four hours under the following conditions:

bulk volume of catalyst
temperature
air rate
steam rate
800 cm³
500° C.
5 litres (S.T.P.)/h
0.1 kg/h

After this treatment the catalyst was impregnated with a nickel nitrate solution in order to incorporate 5% by weight of nickel therein. The impregnated catalyst was dried at 120° C. and calcined in air at 500° C. The resulting nickel oxide was converted to nickel sulphide by a treatment with a H_2—H_2S mixture.

Table VI shows the composition of the resulting reaction product, which was found to be substantially completely saturated.

TABLE VI

Feed	butene-1
Product composition (% by weight) C_1—C_3 hydrocarbons	5.0
branched C_4-hydrocarbons	41.3
unbranched C_4-hydrocarbons	17.4
branched C_5-hydrocarbons	22.3
unbranched C_5-hydrocarbons	0.5
branched C_6-hydrocarbons	8.3
unbranched C_6-hydrocarbons	—
higher hydrocarbons	5.2

The high yields of branched C_1 and C_5 hydrocarbons are particularly advantageous.

EXAMPLE III

Three further experiments were carried out, all with pentene-1 as the starting material. In the first and second experiment the same catalyst as used in Example II was employed, whereas in the third experiment a catalyst was used whose manufacture differed from that of the catalyst employed in Example II only in that the steam-air mixture was passed over the pelleted carrier at 600° C. rather than at 500° C.

The reaction conditions were: pressure: 20 kg/cm², liquid hourly space velocity: 2.0 1/h.1, molar ratio of H_2/pentene-1: 4:1. The reactor inlet temperature in the first experiment was 320° C., in the two other experiments 300° C.

The results are given in Table VII.

TABLE VII

Feed	Pentene-1		
Reactor inlet temperature	320° C.	300° C.	300° C.
temperature during steam/air treatment of catalyst carrier	500° C.	500° C.	600° C.
Product composition (% by weight)			
C_1-C_3-hydrocarbons	2.1	} 17.0	} 15.6
branched C_4-hydrocarbons	12.1		
unbranched C_4-hydrocarbons	1.6		
branched C_5-hydrocarbons	49.3	61.5	47.6
unbranched C_5-hydrocarbons	3.2	5.9	4.2
branched C_6-hydrocarbons	22.4	} 6.0	} 17.5
unbranched C_6-hydrocarbons	1.5		
higher hydrocarbons	7.7	not measured	15.2

EXAMPLE IV

A mixture of propene-1 and hydrogen (molar hydrogen/hydrocarbon ratio = 4:1) was passed over an acidic isomerization catalyst containing nickel sulphide (composition 83.8% by weight of silica, 11.4% by weight of alumina and 4.8% by weight of nickel sulphide) at a total pressure of 20 kg/sq.cm., an inlet temperature of 300° C. and a liquid hourly space velocity of 2 1/h.1.

Table VIII shows the composition of the reaction product after a test period of 5 hours.

TABLE VIII

Composition of final product, % by weight (based on the feed)	
Methane	0.1
ethene and ethane	0.1
propene and propane	30.2
i-butenes and i-butane	41.9
n-butenes and n-butane	0.5
i-pentenes and i-pentane	10.3
n-pentenes and n-pentane	0.2
i-hexenes and i-hexane	13.6
n-hexenes and n-hexane	0.0
higher boiling hydrocarbons	3.0

The Table shows that only very slight quantities of methane and C_2—hydrocarbons are formed, whereas high yields of branched C_4—, C_5— and C_6—hydrocarbons are obtained. It is noticeable that straight-chain hydrocarbons having a higher boiling point than propane and propene are almost entirely absent.

EXAMPLE V

The starting material was a fraction boiling between 35° C. and 100° C. of a gasoline obtained by catalytic cracking. This gasoline was passed over a catalyst containing 83.8% by weight of silica, 11.4% by weight of alumina and 4.8% by weight of nickel sulphide.

Table IX shows the properties of the starting material, the reaction conditions and the properties of the product obtained in the present experiment.

TABLE IX

Reaction conditions		
Inlet temperature, °C.	—	300
pressure, kg/sq. cm.	—	20
liquid hourly space velocity, 1/h. 1	—	1.0
hydrogen/hydrocarbon molar ratio	—	4
Properties of feed and reaction product	Feed	Product
Yield C_5 + % by weight, based on feed	—	90
octane number F—1—1½	98.0	91.5
octane number F—2—1½	84.9	90.7
sensitivity (F—1—1½) — (F—2—1½)	13.1	0.8

As Table IX shows, in the process according to the invention a final product is obtained having a high octane number (F—1—1½ = 91.5) and an excellent sensitivity (0.8).

The yield and octane number were determined of some fractions obtained by distillation of the reaction product obtained. The results are shown in Table X.

TABLE X

Fraction	% by weight of feed	F—1—1½	F—2—1½	Sensitivity
entire product	90	91.5	90.7	0.8
C_5 — 100° C.	80	93.7	92.9	0.8
C_5 — 85° C.	70	96.3	95.8	0.5

Table X shows that fractions having a high (93.7) or very high (96.3) F—1—1½ octane number may be obtained by removing the highest boiling portion from the reaction product.

COMPARATIVE EXAMPLE E

Experiment 5 was repeated with a different catalyst, viz. a conventional non-acidic sulphided cobalt oxide - molybdenum oxide - alumina catalyst (5% by weight CoS, 11% by weight MoS₃, 84% by weight Al₂O₃). The reaction conditions were the same. The yield (C₅⁺% by weight, based on feed) amounted to about 100%, the F—1—1½ octane number to 88.2 and the F—2—1½ octane number to 87.3. The sensitivity equalled 0.9. Comparison of these octane numbers with those listed in Table IX reveals the superiority of the process according to the present invention.

In the catalytically hydrogenative conversion of unbranched or sparsely branched olefins into hydrocarbons having branched or more highly branched hydrocarbon chains respectively, according to the present invention, very high heat effects are found to occur as a result of the exothermic nature of the hydrogenation reactions. The resultant increase in the temperature promotes hydrogenative cracking which is likewise an exothermic reaction. Hence it is difficult to carry out the process on a commercial scale in a reactor with a fixed catalyst when operating on feedstocks that have a high or fairly high olefin content. The conventional method of preventing excessive temperature increases, viz. the subdivision of the catalyst into a number of separate beds connected in series, and cooling the reaction mixture between the beds (this is frequently carried out by injecting liquid reaction products or liquid fresh feed) is unattractive in the present case since the heat effects are so high that excessive temperature increases through the separate beds can only be prevented by using beds having very little depth and this is hardly, if at all feasible from a technical point of view, particularly when the feed material is highly unsaturated.

It has been found, however, that the above-mentioned drawbacks can be obviated in a simple manner by mixing the fresh feed before it is contacted with the catalyst with a certain portion of the product obtained in the conversion. In particular the hydrocarbon mixture obtained in the conversion is recycled in such a quantity that the weight ratio of the recycled hydrocarbon mixture to the fresh starting hydrocarbon mixture is equal to between 0.005 and 0.1 and material is equal to between 0.005 and 0.1 and preferably between 0.015 and 0.05 times the difference between the bromine number of the fresh starting material and the bromine number of the final product.

By "bromine number" in the present specification and claims is meant the McIlhiney bromine number. The determination of the bromine number has been described, inter alia, by C. Zerbe, "Mineralöle und verwandte Produkte", 1952, pp. 201—203.

The fresh feed, the hydrocarbon to be recycled, and the hydrogen-containing gas may, for example, be mixed with each other in a relatively cold state and then (after being passed if desired, through one or more heat exchangers) raised to the desired reaction temperature in a pipe still. This manner of heating may sometimes lead to a relatively rapid fouling of the pipe stills, and this is presumably due to the relatively high content of the olefinic components of the feed. However, this drawback may be obviated by heating the hydrocarbon mixture to be recycled, whether or not mixed with hydrogen-containing gas, to a temperature higher than the temperature at the beginning of the reaction zone and by then mixing the said mixture with the fresh feed and with hydrogen-containing gas (in so far as the latter has not already been added to the hydrocarbons for recycling before the latter were heated), after which the resultant mixture is introduced into the reaction zone without deliberate further heating or cooling. The hydrocarbon stream which is to be recycled is preferably heated to a temperature which is 10° C.—100° C. higher than the temperature at the beginning of the reaction zone. The temperatures and the quantities of the various streams should, of course, be so

adjusted as to ensure that the final mixture has the desired temperature and may be introduced into the reaction zone without deliberate further heating or cooling.

5   This embodiment of the present invention is based on the discovery that the hydrocarbon mixture obtained by the reaction has a considerably increased thermal stability owing to the fact that the said mixture has a low 10 content of olefins, so that it can be readily heated to temperatures which are above the temperature at the beginning of the reaction zone, and that in the present mixing the temperature of the fresh hydrocarbon or hy- 15 drocarbons to be treated cannot susbtantially exceed the temperature of the recycled heated hydrocarbons, while when the said fresh hydrocarbon or hydrocarbons are heated in a pipe still there may be considerably higher local 20 temperatures.

In this embodiment the cold or relatively cold starting material is preferably mixed in a tube, and at a short distance from the reaction zone with the heated hydrocarbons which are 25 to be recycled. This minimizes the drawbacks of any slight fouling since it is obviously much easier to clean such a tube than the complicated systems of narrow pipes, such as are used in pipe stills, etc. With the use of such an 30 arrangement there is little fouling owing to the short distance between the mixing point(s) and catalyst because the mixture is only for a short period subject to conditions which usually promote undesirable reactions. The flow in 35 such a tube may be either of the laminar type or of the turbulent type. Turbulent flow is preferred.

The use of the recycle technique in conjunction with the process according to the 40 present invention, enables the use of one single catalyst bed in the reaction zone, if desired.

It should be noted that when the recycle ratio is increased, the temperature to which the stream to be recycled should be heated 45 decreases, as a result of which the maximum possible temperature occurring during mixing is lower, and in addition the temperature increase during the reaction is less pronounced. But economic factor limit the increase of this 50 ratio. It is immaterial in which order the hydrocarbon oils, the hydrogen-containing recycle gas and the gas-containing fresh hydrogen are mixed.

The recycle technique will now be elucidated 55 with reference to the accompanying drawing in which figure 1, schematically shows a preferred embodiment.

Referring to figure 1, 1 designates the line through which the fresh feed is supplied. After 60 being mixed with the hydrogen-containing gas supplied through line 2 and with the heated reaction product in the vapour phase which is supplied through line 3, the reaction mixture flows through the line 4 to the reactor. The 65 catalytic conversion takes place in the reactor

5 containing the catalyst bed 6 and is attended by a slight temperature increase. The reactor effluent flows from the cooler 7 to the gas/liquid separator 8. The liquid separating is passed off through line 9 and partly recycled 70 through line 3 (which is provided with a pump 10 and the still 11) to the reactor, the remaining portion being passed off through line 12. The recycled stream is vapourised in the still 11 and heated to a temperature sufficiently 75 higher than the temperature at the beginning of the reactor to enable the fresh feed to be vapourised and raised to the reaction temperature. The liquid passed off through line 12 is worked up in the conventional manner for the 80 recovery of the refined oil (for example by further expansion in a low-pressure separator (not shown), followed by stripping and/or distillation).

Hydrogen-containing gas leaving the separ- 85 ator 8 is recycled through line 2, compressor 13 and still 11. Gas-containing fresh hydrogen is supplied through line 14. If desired, a bleed stream may be withdrawn through line 15.

The following example sets out an embodi- 90 ment of the present invention employing the above recycle technique.

Example VI

The starting material was a fraction from a gasoline obtained by catalytic cracking, which 95 fraction had a boiling range between 38° C. and 91° C. (ASTM) (upper cutting point about 100° C.). This fresh feed had an F—1 —1½ octane number of 99.2 and an F—2—1½ octane number of 85.7 and contained 62% by 100 weight of olefins, 1% by weight of aromatics and 37% by weight of saturated compounds. The bromine number was 110. This material was treated in accordance with the present invention in a unit of the type shown in figure 1. 105

The catalyst used was nickel sulphide incorporated on a silica-alumina cracking catalyst (5 parts by weight of nickel per 100 parts by weight of cracking catalyst which comprised 13% by weight of Al_2O_3, 87% by weight of 110 SO_2). This catalyst was present in the form of a single bed, viz. in a quantity of 250 ml. The quantity of fresh feed was 250 ml per hour (measured in a liquid state). The pressure at the beginning of the reactor was 60 atm.; the 115 temperature immediately before the catalyst bed 300° C., and immediately thereafter 352° C. The temperature in the separator 8 was 15° C. The liquid separating in the separator was partly recycled through line 3 in a quantity 120 of 3.07 parts by weight per part by weight of fresh feed. This stream was heated in the still 11 to 375° C. Sufficient hydrogen-rich gas was supplied through line 2 to bring the molar ratio of hydrogen to hydrocarbons in the re- 125 actor feed to 2.5. The temperature of the fresh feed supplied through line 1 was 27° C., that of the gas supplied through line 2, 375° C. The product discharged through line 12 was worked up in the conventional manner. The resultant 130

gasoline was practically free from olefins (bromine number <1) and had an F—1—1½ octane number of 94.2 and an F—2—1½ octane number of 92.5.

5 The problem of avoiding large temperature increases in fixed catalyst beds and fouling of heating equipment may, if desired, be solved in other ways, e.g. by employing a finely divided fluidized catalyst rather than a fixed
10 catalyst.

When using a fluidized catalyst mass the temperature is substantially equal throughout the whole bed, moreover, the olefinic starting material and the hydrogen-containing gas need
15 only to be heated to rather low temperatures. Thus, in a particular case, when operating at a reactor temperatures of 270° C.—300° C., it was found that the two streams needed to be heated to about 50° C. only. When using a
20 fluidized catalyst the space velocity will usually be in the order of 0.5—20 kg olefinic starting material/hour/kg catalyst.

When operating on feedstocks that do not give rise to large temperature increases but
25 that on the other hand cause rapid fouling of conventional tubular furnaces and steam heaters, another technique for bringing the fresh feed to reaction temperature may be attractive.

30 In this technique the reaction mixture which leaves a reaction zone, or a portion of the said reaction mixture, is heated to a temperature higher than the temperature at the beginning of the first (which may be the only) reaction
35 zone, and is then indirectly heat-exchanged with the fresh oil which is to be treated, to which, if desired, hydrogen-containing gas may already have been added, after which the oil for treatment thus heated, after mixing with
40 hydrogen-containing gas in so far as the latter has not already been added before indirect heat-exchange, is introduced without deliberate further heating or cooling into the first reaction zone.

45 This technique is again based on the observation that the oil already treated has obtained such a high thermal stability that it can be redily heated to temperatures substantially above the temperature prevailing at the begin-
50 ning of the first, which may be the only reaction zone, and in addition, that in the heat exchange according to the invention the hydrocarbon oil for treatment cannot exceed the temperature of the heated reaction mixture
55 whereas when heating takes place in a pipe still or steam heater there may be considerably higher local surface temperatures.

In order to bring the feed of the first reaction zone to the reaction temperature this
60 feed is heat-exchanged with the reaction mixture (or a portion thereof) leaving one of the reaction zones. If more than one reaction zone is used either the mixture leaving the first reaction zone or the mixture leaving one of the
65 other reaction zones may be used. The reaction mixture leaving the first reaction zone (or portion thereof) is preferably used for bringing the fresh feed to the reaction temperature.

The reaction mixture or portion thereof used
70 for the indirect heat-exchange with the feed is first heated to a temperature which is higher, preferably 10° C. to 50° C. higher, than the temperature at the beginning of the first reaction zone, after which it is indirectly heat-
75 exchanged with the feed to be treated, and this may take place for example in one or more heat exchangers. If desired, hydrogen-containing gas may already have been added to this oil. The fresh hydrocarbon oil or the mix-
80 ture thereof with hydrogen-containing gas may be slightly pre-heated if desired, but obviously only to a temperature lower than the inlet temperature in the first reaction zone.

The heated oil is then mixed with hydrogen-
85 containing gas in so far as the latter has not already been added before the indirect heat exchange, after which it is introduced without deliberate further heating or cooling into the first, which may be the only, reaction zone.
90 This hydrogen-containing gas may or may not have been preheated. The temperatures and the quantities of the various streams should, of course, be so adjusted as to ensure that the final mixture has the desired temperature.

95 The entire reaction mixture leaving a certain reaction zone is preferably used for heating up the fresh feed, since in this case the surface temperatures in the indirect heat exchange zone are lowest. It is, however, also possible to
100 employ a portion of such a mixture for the heating up, for example, only the refined oil separated from such a mixture. The heating operation of the stream to be used for the heat exchange to a temperature higher than the
105 temperature at the beginning of the first reaction zone may be carried out in a conventional manner, for example in one or more heat exchangers, steam heaters and/or pipe stills; in this case the risk of fouling is very
110 slight since the product heated is already stabilised.

The heating technique just discussed will now be illustrated with reference to figure 2 of the accompanying drawing.

115 Referring to figure 2, 1 designates the line through which the oil to be treated is supplied. This oil after being mixed with hydrogen-containing gas supplied through line 2, flows through the line 3 and the heat exchanger 4
120 to the reactor 5. The mixture is brought to the desired reactor inlet temperature in the heat exchanger by indirect heat exchange with the reaction product of which the temperature has been increased. The hydrogenative treatment
125 of the oil takes place in the reactor in which the catalyst beds 6, 6¹, 6¹¹, 6¹¹¹ are provided, and will be attended by a certain rise in temperature. The reactor effluent flows through line 7 which is provided with the steam heater
130 8, the heat exchanger 4 and the cooler 9, to

the gas/liquid separator 10. This steam is heated in the steam heater 8 to a temperature higher than the temperature at the beginning of the reactor, and the stream thus heated is used in heat exchanger 4 to bring the fresh feed to the reaction temperature. The hydrogen-containing gas leaving the separator 10 passes through line 11 and compressor 12 to line 2 and is there mixed with fresh hydrogen-containing gas supplied through line 13. The liquid separating is passed off through line 14 and worked up in the conventional manner for recovering the treated oil (for example by further expansion in a low pressure separator (not shown) followed by stripping or distillation). A portion of the oil passed off through line 14 may be recycled to the reactor as cooling oil, viz. through line 16 and pump 17. In this case it is injected between the beds and prevents an excessive rise in temperature in the reactor.

WHAT WE CLAIM IS:—

1. A process for the catalytic conversion of unbranched or sparsely branched hydrocarbons into hydrocarbons having a branched or more highly branched carbon chain respectively, which comprises contacting an olefinic starting material at elevated temperature and pressure and in the presence of hydrogen or a hydrogen-containing gas with a solid acidic isomerization catalyst on which are supported one or more sulphides, selenides, tellurides, antimonides and/or arsenides of the metals of the left-hand column of Group VI and/or one or more sulphides, selenides, tellurides, antimonides and/or arsenides of the metals of Group VIII of the Periodic Table.

2. A process as claimed in claim 1, wherein the starting material consists of or contains one or more olefins having from 3 to 8 carbon atoms per molecule.

3. A process as claimed in claim 1 or 2, wherein the starting material consists of or contains one or more olefins having from 4 to 8 carbon atoms per molecule.

4. A process as claimed in claim 1 or 2, wherein the starting material is propene.

5. A process as claimed in any one of claims 1—3, wherein the olefinc starting material is a gasoline obtained by catalytic cracking or a fraction thereof.

6. A process as claimed in claim 5, wherein the starting material used is the lower-boiling fraction of a gasoline obtained by catalytic cracking, which fraction has an upper cutting point of from 80° C. to 130° C.

7. A process as claimed in any one of claims 1—6, wherein the acidic isomerization catalyst is a silica-alumina catalyst, preferably having a silica content of at least 60% by weight.

8. A process as claimed in any one of claims 1—7, wherein the total catalyst contains 0.5 —15% by weight of metal sulphides, selenides, tellurides, arsenides and/or antimonides.

9. A process as claimed in any one of claims 1—8, wherein the catalyst contains nickel sulphide and/or cobalt sulphide.

10. A process as claimed in any of claims 1—9, wherein the conversion is effected at a temperature in the range of from 100° C. to 500° C.

11. A process as claimed in claim 10 wherein the temperature is in the range of from 200° to 500° C.

12. A process as claimed in claim 10, wherein the temperature is in the range of from 200° C. to 400° C.

13. A process as claimed in claim 5, wherein the conversion is effected at a temperature in the range of from 250° C. to 450° C.

14. A process as claimed in any one of claims 1—13, wherein the conversion is effected at a total pressure in the range of from 10 to 100 atm.

15. A process as claimed in any one of claims 1—14, wherein the hydrogen partial pressure is at least 5% of the total pressure.

16. A process as claimed in any one of claims 1—15, wherein the hydrogen partial pressure is at least 50% of the total pressure.

17. A process as claimed in any one of claims 1—16, wherein the catalyst comprises a silica-alumina compound having a silica content of at least 60% by weight, based on the total catalyst and on which is supported 1—10% by weight of nickel sulphide, based on the total catalyst.

18. A process as claimed in any one of claims 1—17, wherein the hydrocarbon mixture obtained in the conversion is recycled in such a quantity that the weight ratio of the recycled hydrocarbon mixture to the fresh starting material is between 0.005 and 0.1 times the difference between the bromine number of the fresh starting material and the bromine number of the final product.

19. A process as claimed in claim 18, wherein the said weight ratio is between 0.015 and 0.05.

20. A process as claimed in claim 18 or 19, wherein the hydrocarbon mixture to be recycled, whether or not mixed with hydrogen-containing gas, is heated to a temperature which is higher than the temperature at the beginning of the reaction zone and then mixed with the fresh feed and with hydrogen-containing gas (in so far as the said gas has not already been added to the hydrocarbons for recycling before the latter were heated), after which the resultant mixture is introduced into the reaction zone without deliberate further heating or cooling.

21. A process as claimed in claim 20, wherein the hydrocarbon stream to be recycled is heated to a temperature which is 10° C. to 100° C. higher than the temperature at the beginning of the reaction zone.

22. A process as claimed in any one of claims 1—17, wherein the reaction mixture leaving a reaction zone, or a portion of the said

reaction mixture, is heated to a temperature higher than the temperature at the beginning of the first, which may be the only, reaction zone, and is then indirectly heat-exchanged with the fresh oil which is to be treated, to which, if desired, hydrogen-containing gas may already have been added, after which the oil for treatment, thus heated, after mixing with the hydrogen-containing gas in so far as the latter has not already been added before the indirect heat exchange, is introduced without deliberate further heating or cooling into the first, reaction zone.

23. A process as claimed in claim 22, wherein the reaction mixture leaving the first reaction zone, or a portion thereof, is used for bringing the fresh feed to the reaction temperature.

24. A process as claimed in claim 22 or 23, wherein the reaction mixture or the portion thereof used for the indirect heat exchange with the feed is first heated to a temperature which is 10° C. to 50° C. higher than the temperature at the beginning of the first reaction zone.

25. A process as claimed in any one of claims 22—24, wherin the entire reaction mixture leaving a certain reaction zone is used for heating up the fresh feed.

26. A process for the catalytic conversion of unbranched or sparsely branched olefins into hydrocarbons having branched or more highly branched carbon chains respectively as claimed in claim 1 substantially as hereinbefore described.

27. A process for the catalytic conversion of unbranched or sparsely branched olefins into hydrocarbons having branched or more highly branched carbon chains respectively as claimed in claim 1, substantially as hereinbefore described, with particular reference to Examples I to VI.

28. A process for the catalytic conversion of unbranched or sparsely branched olefins into hydrocarbons having branched or more highly branched carbon chains respectively as claimed in claim 1, substantially as hereinbefore described, with particular reference to the drawings.

29. Hydrocarbons and hydrocarbon mixtures whenever obtained by the process as claimed in any one of the preceding claims.

30. A process for the production of gasoline and gasoline components, wherein the product or a portion thereof, obtained by the process as claimed in any one of claims 1—28, is blended with one or more other gasoline components.

31. A process for the production of gasolines and gasoline components as claimed in claim 30, susbtantially as hereinbefore described.

32. Gasolines whenever obtained with the use of the process as claimed in claim 30 or 31.

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Fig. 1

Fig. 2